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Stoichiometry-induced roughness on antimonide growth surfaces

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Phase shifts in the intensity oscillation of reflection high-energy electron diffraction spots provide evidence for monolayer island formation on AlSb that is caused by sudden changes in surface stoichiometry. High-resolution scanning tunneling microscopy confirms the interpretation of the phase shift. These results are consistent with a previous structural assignment of the AlSb $\beta(4 \times 3)$ and $\alpha(4 \times 3)$ surface reconstructions and provide guidelines for producing smooth interfaces in antimonide-based heterostructures. [DOI: 10.1063/1.1366360]

Most III–V materials exhibit (001) surface reconstructions with group III and group V compositions that differ from the bulk material. These stoichiometries are an intrinsic source of roughness at heterointerfaces, because the extra or missing atoms on the surface of the initial material must be accommodated by the subsequently grown material. Monolayer-scale interface roughness may be particularly important for devices such as resonant tunneling diodes, which have barriers that can be as thin as a few monolayers. In order to optimize process measurement and control techniques for growth of device heterostructures, one may therefore need to consider the detailed stoichiometry of compound semiconductor surfaces.

Stoichiometry-induced roughness has been discussed previously in connection with the $\beta 2(2 \times 4)$ surface reconstruction of GaAs (001) and InAs (001). When the $\beta 2(2 \times 4)$ surface is cooled under a constant arsenic flux, monolayer islands form as the surface converts to the more arsenic-rich $c(4 \times 4)$ reconstruction.^{1,2} Roughness formation has been observed at a heterointerface when an antimonide (AlSb or GaSb) is grown on the InAs $\beta 2(2 \times 4)$ surface.³ Standard In–Sb interface preparation techniques yield an interface with 1/4 monolayer (ML) of vacancy islands, due to the incomplete indium coverage (3/4 ML) of the starting InAs surface reconstruction.

This work addresses a subtle stoichiometry issue in AlSb homoepitaxy with important consequences for producing high quality heterointerfaces in antimonide-based device structures. AlSb belongs to the 6.1 Å family of compound semiconductors (AlSb, GaSb, InAs, and alloys), which shows great promise for applications such as infrared detectors, lasers, high-speed electronics, and spin-based devices.⁴ The antimonides present unique growth challenges because of their unusual surface reconstructions, which contain more than a full layer of antimony atoms.^{5,6} We have used reflection high-energy electron diffraction (RHEED) oscillations and scanning tunneling microscopy (STM) to probe monolayer island formation that results from changes in the

stoichiometry of antimonide surface reconstructions under typical growth conditions.

Using a combination of high-resolution STM and *ab initio* theory, we have shown previously that four distinct AlSb reconstructions exist for typical substrate temperatures and antimony fluxes.⁵ Here we consider the two surfaces that are most likely to be encountered during growth, designated $\beta(4 \times 3)$ and $\alpha(4 \times 3)$. Their aluminum content differs by 1/4 ML, and it is this difference that is responsible for the roughening that we detect with RHEED and STM. Figure 1(a) shows STM images of the AlSb $\beta(4 \times 3)$ and $\alpha(4 \times 3)$ surface reconstructions. The β surface exists for most conventional growth conditions: substrate temperatures of 450–550 °C, growth rates around 1 ML/s and a Sb:Al atomic flux ratio of 2:1. The top layer of each $\beta(4 \times 3)$ unit cell contains three antimony dimers (bright elongated beads) and

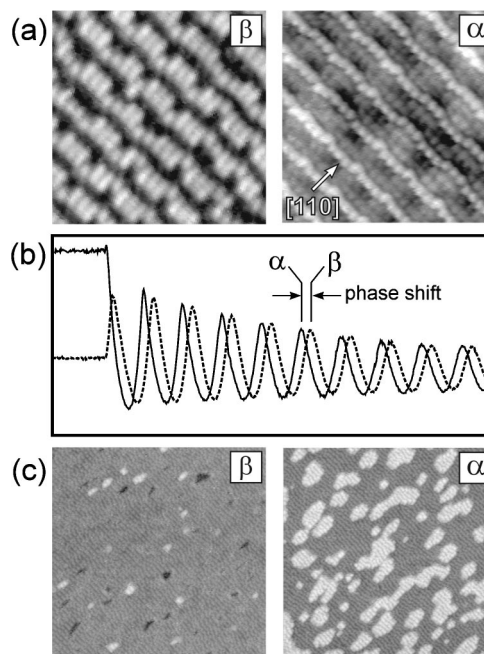


FIG. 1. (a) Filled state STM images (8 nm \times 8 nm) of AlSb $\beta(4 \times 3)$ and $\alpha(4 \times 3)$ surface reconstructions. (b) RHEED oscillations for growth on flat $\beta(4 \times 3)$ and $\alpha(4 \times 3)$ starting surfaces. (c) Filled state STM images (74 nm \times 74 nm) of 1 ML AlSb grown on flat $\beta(4 \times 3)$ and $\alpha(4 \times 3)$ starting surfaces. Both surfaces in (c) have a $\beta(4 \times 3)$ reconstruction; the grayscale levels correspond to 3 Å monolayer-height features.

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one Al–Sb “heterodimer,” all on top of a full layer of Sb atoms. The surface stoichiometry is thus 1–7/12 ML Sb and 1/12 ML Al. The α surface results from higher substrate temperatures, lower fluxes, or lower Sb:Al ratios; it contains only Al–Sb heterodimers, yielding a stoichiometry of 1–1/3 ML Sb atoms and 1/3 ML Al atoms in the final layers. The assignment of these structures and the experimental details of the STM work are addressed in Ref. 5.

AlSb buffers (≥ 700 nm) were grown on GaSb substrates at 550–600 °C and 1 ML/s, and then flat α or β surfaces were prepared for subsequent experiments. The β surface was prepared by growing AlSb at 1/10 ML/s for 1 min around 600 °C, annealing for 1 min under a flux of Sb₄ (~ 0.2 ML/s), then cooling to 520 °C in 200 s. The α surface was prepared by additionally annealing the surface at 520 °C *without* a Sb₄ flux. For RHEED measurements, a 10 kV electron beam was incident on the sample surface between 1.5° and 2.5°. The beam had been previously adjusted to focus on the phosphor screen (~ 70 cm from electron gun to screen) without the sample in place. Both surface reconstructions give (1×3) RHEED patterns. The distinguishing feature of the RHEED pattern for the α surface is an arch of sharp $3 \times$ spots ($[\bar{1}10]$ direction) in the first Laue zone, which results from strong row ordering of the Al–Sb heterodimers. The corresponding β pattern is usually much streakier. If special care is taken to order the reconstructions, $3 \times$ spots may also be observed for the β surface, and both α and β can exhibit weak $4 \times$ streaks in the $[110]$ direction. For this work, we did not attempt to obtain this higher degree of ordering.

Oscillations in the intensity of individual RHEED spots track the addition of single layers of new material. For III–V semiconductor growth, this feature is routinely used to calibrate group III atomic fluxes, which typically govern III–V growth rates. The traditional interpretation of RHEED oscillations holds that the electron scattering probability is modulated by the evolution of monolayer surface morphology during growth.^{7,8} However, the absolute phase of the RHEED oscillations with respect to the phase of the evolving surface morphology remains a topic of ongoing research.^{8,9} The absolute phase depends sensitively on scattering geometry. In the present work, the effects of surface stoichiometry are manifest in phase *shifts* between RHEED traces obtained under identical scattering geometries, but with different starting surface reconstructions.

Two AlSb homoepitaxy experiments [Figs. 1(b) and 1(c)], taken together with the structural assignments of Ref. 5, clearly show the role that stoichiometry plays in interface roughness formation. The oscillations in Fig. 1(b) were obtained by growing AlSb starting with flat $\beta(4 \times 3)$ and $\alpha(4 \times 3)$ surfaces at 520 °C and 0.1 ML/s, while monitoring the RHEED specular spot intensity. Following clarification of several details, we will argue that the phase shift between the RHEED traces results from the difference in aluminum content of the starting $\beta(4 \times 3)$ and $\alpha(4 \times 3)$ surfaces.

During each measurement series, the RHEED scattering geometry was kept constant by monitoring a single diffraction spot and by rigidly fixing the substrate rotation control. To confirm that we are truly observing a growth phenomenon, we have shown in separate experiments that the phase

shift between the β and α starting surfaces does not depend on the polar or azimuthal angle of the electron beam or on which diffraction spot is monitored.

As discussed by Braun *et al.*,^{8,10} the oscillation phase at the start of growth may evolve in a way that depends on a combination of diffraction geometry and changing surface composition. In Braun’s work on heteroepitaxy, gallium segregation into AlAs (AlAs on GaAs) produced a phase shift that evolved in a geometry dependent way over many monolayers, relative to homoepitaxial growth (AlAs on AlAs).¹¹ However, once segregation was finished, the “saturation value” of the phase shift always reflected the true shift in the phase of AlAs growth. This saturation value is reached rapidly in our homoepitaxy experiments under an excess antimony flux. Following a brief transient within the first monolayer, both the α and β starting surfaces are transformed into growing β surfaces, and we need not be concerned with a compositional transition regime. We have confirmed this fact by extensive RHEED and STM studies of the submonolayer growth regime for AlSb.

Given these considerations, the observed phase shift between RHEED traces for α and β starting surfaces must represent a real difference in the phase of the oscillatory evolution of monolayer surface roughness during growth. Significantly, the oscillations for the α starting surface lead those for the β surface by approximately 1/4 monolayer. This shift is a consequence of the extra aluminum contained in the α starting surface. Under the Sb-rich conditions of growth, where the α surface converts to β , the extra aluminum forms islands in the next highest layer and gives it a 1/4 ML head start over growth on the β starting surface.

We see further evidence for this interpretation in STM images of postgrowth surfaces. Figure 1(c) shows two growths of 1.00 ± 0.02 ML AlSb (previously calibrated by RHEED oscillations) onto flat surfaces of either α or β reconstructions at 520 °C. Growth on β gives a nearly flat surface with equal areas of small monolayer islands and pits, consistent with a complete added layer of AlSb. An identical growth on the α starting surface contains monolayer islands and has clearly overshot a single new layer by about 1/4 ML. In an analogous experiment (not shown), we have exposed the flat α surface at 450 °C to a Sb₄ flux for a few seconds, converting it to a β reconstruction. The excess aluminum of the original α surface produces roughly 1/4 ML of AlSb islands on the resulting β surface.¹²

The RHEED phase shift can be used to monitor the rate of conversion from $\beta(4 \times 3)$ to $\alpha(4 \times 3)$. Figure 2 shows the phase shift as a function of the time that the initial flat β surface is annealed at 520 °C without an antimony flux. The phase shift is measured relative to the oscillations for growth on the β surface, i.e., for an unannealed surface. The phase shift increases rapidly at first, and eventually levels out around 0.3 ML, slightly higher than the 1/4 ML difference expected between perfect β and α surfaces. This slight excess is not surprising, as our imperfect experimental surfaces are unlikely to have exactly the stoichiometry of the ideal theoretical surfaces.⁵ To explain the measured maximum phase shift, the disordered β surface that exists under Sb₄ at 520 °C should have a lower aluminum content than predicted for the theoretical surface, or the α surface produced by an-

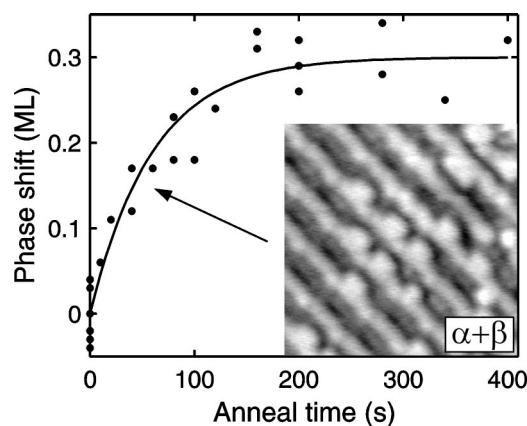


FIG. 2. Phase shift of fifth RHEED oscillation maximum for growth of AlSb as a function of $\beta(4 \times 3)$ pregrowth anneal time at 520 °C. An increasing phase shift corresponds to a higher proportion of the $\alpha(4 \times 3)$ reconstruction in the starting surface. The curve is a guide to the eye. The inset shows a STM image of a mixed $\alpha + \beta$ surface (8 nm \times 8 nm) produced by a 40 s anneal.

nealing at 520 °C should have a higher content than predicted. Similar deviations from ideal stoichiometries were observed for the GaAs $c(4 \times 4)$ reconstruction.^{2,13}

An anneal time of about 40 s is required to reach half of the maximum phase shift, and the corresponding STM image shows a mixture of the β and α structures (Fig. 2 inset). This is the characteristic time required for conversion of $\beta(4 \times 3)$ to $\alpha(4 \times 3)$ through antimony desorption and rearrangement of aluminum atoms. As expected, a surface annealed for 200 s contains exclusively the α reconstruction (image not shown). We have also observed that the intensity of the RHEED specular spot in the $3 \times$ pattern ($[1\bar{1}0]$ incident electron beam) evolves on a time scale comparable to the anneal-time dependence of the phase shift, although the details of this evolution of course depend sensitively on the scattering geometry. The weak $3 \times$ streaks of the β surface evolve into sharp spots in a similar time, consistent with the strong tendency for the α surface to form well-ordered $3 \times$ rows of Al–Sb heterodimers.

The results reported here provide qualitative support for the structural assignments in Ref. 5. In that work, the agreement between STM images and theoretical simulations provided strong evidence in support of the proposed $\alpha(4 \times 3)$ and $\beta(4 \times 3)$ structures. The present work provides a direct experimental measurement of the stoichiometry difference between the two surfaces, and thus makes an even stronger case for the previously proposed structures.

From a practical perspective, the results provide guidelines for avoiding rough interfaces in antimonide-based heterostructures. A growth scenario in which α -to- β roughening would be important is when two separate antimony cells with different fluxes are desired. This situation arises during growth of a resonant tunneling diode structure containing $\text{Al}_{0.9}\text{Ga}_{0.1}\text{Sb}$ barriers (0.5 ML/s) and a GaSb well (0.05 ML/s).¹⁴ Growth interrupts under the lower antimony flux could give an α or mixed $\alpha + \beta$ surface, leading to monolayer islands upon switching to the higher fluxes under which the β surface prevails. Similarly, when the α surface exists

during growth—a relatively Sb lean but not unreasonable growth environment—then growth interrupts may produce islands if the β surface forms. Note that α -to- β roughening should also occur on GaSb, but at temperatures around 100 °C lower than for AlSb, i.e., in the most common antimonide device growth temperature range (400–500 °C). We have also seen evidence of stoichiometry-induced roughening when growth involves the AlSb $\beta(4 \times 3)$ surface and growth interrupts produce the more Sb-rich reconstructions $\gamma(4 \times 3)$ or $c(4 \times 4)$, which exist under normal growth conditions for some devices.

We have shown that one can expect roughening when there are sudden changes between surface reconstructions of different stoichiometry. This effect is technologically relevant when two or more reconstructions exist within typical device growth temperature and flux ranges, as is true for the antimonides, and matters most during homoepitaxial growth interrupts prior to heterointerface formation. RHEED and STM data independently give explicit evidence of this roughening mechanism and provide a semiquantitative means to measure the stoichiometry difference between two surface reconstructions.

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